Near-field Stimulated TOF Nanometric Surface Mass Spectroscopy;
Characterization of Nano-Localized Surfaces

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A novel methodology that provides direct nano-localized measurements of the atomic mass on surfaces has been developed. Using an original UHV-STM system, we could locally ionize surface atoms by irradiating the combination pulses of an optical laser beam and an electron beam emitted from the STM probe tip. Then the desorbed ions were collected, accelerated and detected by a Time of Flight Mass Spectrometer (TOF- MS).

1. Near-field Stimulated TOF Nanometric Surface Mass Spectroscopy.

With STM it is possible to obtain topological information of a surface with nanometric resolution. Detected images contain structural data that give the researcher several clues on the chemical compositions of the sample. However, no direct knowledge of the atomic or molecular species is available. This fact implies that the interpretation of STM images is not a straightforward process and in many cases deep theoretical investigation is necessary to elucidate the structures detected. In several applications, as nano-technology or semiconductor devices fabrications, it is important to know what atomic species is forming the structures examined by STM. We focused on these problems to newly develop laser assisted STM/TOF mass spectrometer integrated system that allows conventional STM imaging and simultaneous mass analysis.
In the laser assisted STM/TOF hybrid mass analyzer, an STM probe tip is used not only as a probe to image the sample surface but also as an electron beam source. A pulse voltage is applied in the proximity region between the STM tip and the sample. Atoms or molecules in the nano-local area under the STM probe tip are extracted and ionized consequently. To improve the efficiency of extraction and ionization, an optical pulse laser beam is irradiated by synchronizing with an electron beam pulse. The optical laser pulse brings the atoms on an exited state by assisting and facilitating the process of ionization induced by the electron beam pulse. Then the desorbed ions are analyzed by a TOF-MS spectrometer. The laser beam is irradiated through a quartz window attached at the STM chamber. The TOF-MS spectrometer is equipped at the reverse position to the laser window of the STM chamber. All the chambers are kept under an ultrahigh vacuum of 2×10^{-10} Torr by using a turbo-pump, an ion pump and a titanium sublimation-pump.
The TOF-MS spectrometer is composed by a collector, an accelerato, a flight drift chamber and a micro-channel plate detector. The collector is installed in the proximity of the sample surface, and it sends the desorbed ion to the accelerator efficiently. The free flight tube is long stainless steel tube. The micro-channel plate with a voltage of -2.5kV is placed at the end of this tube. The signal amplified by the micro-channel plate is recorded by a digital-oscilloscope. Measurement is done by using a Nd-YAG pulse laser and a pulse voltage generator. The mass/charge ratio is given in proportion to the square of the total flight time.

2. Characterization of nano-localized surface of gold deposited silicone surface.

A typical example of mass analysis of the nano-locarized surface of Au-deposited Si(111) substrate will be presented. The sample was prepared by vacuum evaporation of Au on Si(111) substrate. The sizes of the clusters observed were ca. 20nm. After STM observation, the tip was placed over the cluster interested and an electric pulse (8V, 100 ns) was applied synchronized with an optical laser pulse (266 nm, 5 ns). Then the TOF-MS analysis of desorbed ions contained in the cluster was carried out. The TOF signals due to gold and silicone oxides were detected from the cluster. The STM image was observed again after the TOF-MS analysis. By comparing these two images, it can be clearly understood that the cluster was completely desorbed and analyzed.
In conclusions, the proposed laser assisted STM/ TOF hybrid mass spectroscopy provides a simple but powerful method that can be used efficiently in association with the conventional STM or AFM studies. This novel mass analyzer system has great features such as *in situ* measurement of nano-localized area on the sample surface, simultaneous STM and TOF operations, surface mass analysis with a space resolution of better than 5 nm and a mass resolution of 200 on silicon.
The direct and real time analysis of the atomic or molecular compositions of the complex surfaces such as semiconductors, electrodes or membranes will be comprehensibly available for nanometric characterization of the numerous material surfaces in such fields as electrochemistry, bioelectrochemistry, solid state chemistry and fundamental surface chemistry.

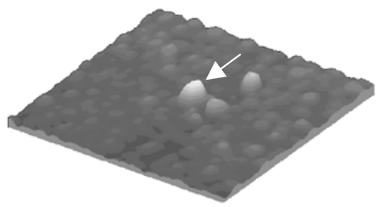

Fig. 1. STM image Au coated Si surface before TOF-MS analysis. Scan size; 300 nm^2

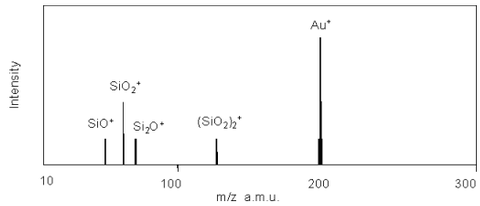

Fig. 2. TOF-MS spectrum of the desorbed cluster.

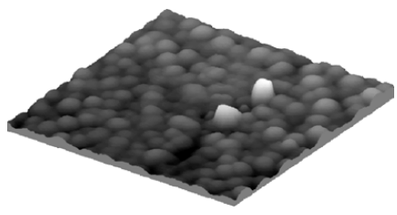

Fig. 3. STM image of Au coated Si surface after TOF-MS analysis. Scan size; 300 nm^2